

B36

RESERVE COPY
PATENT SPECIFICATION
NO DRAWINGS

994377



994377

Date of Application and filing Complete Specification March 9, 1962.
No. 9114/62.
Two Applications made in United States of America (Nos. 95,793 and 95,794),
on March 15, 1961.
Complete Specification Published June 10, 1965.
© Crown Copyright 1965.

Index at acceptance: —C2 C3A11; C5 F1; E1 F(31F, 44)
Int. Cl.: —C 07 c//C 10 m, E 21 b, d

COMPLETE SPECIFICATION
Substituted Ammonium Humate and Process of Making
Same

We, NATIONAL LEAD COMPANY, a corporation organised under the laws of the State of New Jersey, United States of America, of 111 Broadway, New York 6, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —
This invention relates to organic derivatives of humic acid and to processes of making the same. More particularly, the invention relates to long-chain ammonium salts of humic acid, and to the use thereof in well-working operations.
Humic acid is a material of wide distribution, being present in soils, peat and coals, especially coals of the type known as lignite (brown coal). Although the exact details of its chemical structure are not completely known, it is a surprisingly uniform substance considering the variety of source materials of which it represents a natural product of degradation, e.g. leaves, wood, and like vegetable organic matter. It is an acid, in which both carboxyl and phenolic hydroxyl groups contribute base-combining ability. It is soluble in alkalies, e.g. caustic soda and sodium carbonate, has a deep brown colour, and is readily soluble in water when converted to its alkali metal salt, which may be then termed an alkali metal humate, the commonest example of which is sodium humate.
As indicated, it is present in soils and peat, and may readily be extracted from these by known means, most commonly by treatment with dilute aqueous alkali. Whenever it is a matter of producing a commercial humate, that is, whenever economic considerations are of importance, then the humic acid is nearly always derived from its richest common source, which is lignite, of which there are vast deposits

distributed throughout the world, including the United States, and particularly the States of North Dakota, Texas, New Mexico, and California.
Lignite is indeed such an inexpensive commodity that its widest use is as a fuel. However, extraction of its alkali-soluble portion, termed the humic acid fraction, results in a material of considerable usefulness in technology. Humic acid, and its common salt, sodium humate, are, for example, useful as dispersants in aqueous systems, e.g. clay-water systems. Again, these materials are widely used as inexpensive dyes in the paper art. They find application as components of lead storage battery plates, and diverse other uses are known. However, the generally known commercial uses of humates are in aqueous systems, which eliminates large areas of chemical technology as fields for the possible employment of humates.
Specially, the present invention provides a substituted ammonium humate having the formula $R_1R_2R_3R_4N^+Hu^-$ in which Hu^- is the anion of humic acid and in which at least one of the R's is an alkyl or alkenyl radical having from 12 to 22 carbon atoms in a straight chain, and in which those R's which do not have from 12 to 22 carbon atoms in a straight chain comprises hydrogen, alkyl radicals having fewer than 12 carbon atoms, phenyl or benzyl, or two of the R's form a carbon ring including N heterocyclically and bearing said 12 to 22 carbon alkyl or alkenyl radicals, and wherein when two of the R's form a nitrogen-containing heterocyclic ring one of the remaining R's additionally may be a hydroxyalkyl or phenyl-substituted hydroxyalkyl group.
The present invention also provides the process of preparing a substituted ammonium humate as herein before defined characterised by the fact that an appropriate substituted

ammonium ion having the formula $R_1R_2R_3R_4N^+$, is caused to react with a negative humate ion so as to form the said substituted ammonium humate.

In accordance with an illustrative embodiment of our invention, we produce, by methods more specifically hereinafter described, a salt of humic acid, viz., a humate, in which the cation is a substituted ammonium ion, in which one or more of the hydrogen atoms originally present in the ammonium ion is substituted by an alkyl radical, and in which at least one of the said alkyl radicals has from 12 to 22 carbon atoms in a straight chain. It will be clear that the valence positions of the nitrogen atom which are not occupied by hydrogen atoms may be either long alkyl chains, of the type just described, or may be short alkyl chains, from C_1 to C_{11} , that is, methyl to undecyl, or phenyl or benzyl radicals, as long as at least one straight chain alkyl radical is present in the range of C_{12} to C_{22} , which in the methane series corresponds to dodecyl to docosyl.

Typical of the compounds which fall within the scope of our invention are those set forth in the following table:

TABLE I

30	Dodecyl ammonium humate
	Stearyl ammonium humate
	Oleyl ammonium humate
	Palmityl ammonium humate
	Docosyl ammonium humate
35	Methyl dodecyl ammonium humate
	Methyl stearyl ammonium humate
	Di-dodecyl ammonium humate
	Lauryl stearyl ammonium humate
	Butyl docosyl ammonium humate
40	Benzyl lauryl ammonium humate
	Dimethyl lauryl ammonium humate
	Methyl lauryl stearyl ammonium humate
	Tri-lauryl ammonium humate
	Diphenyl stearyl ammonium humate
	Trimethyl lauryl ammonium humate
45	Benzyl diethyl docosyl ammonium humate
	Phenyl dibutyl octadecyl ammonium humate
	Dimethyl dioctadecyl ammonium humate
	Benzyl butyl lauryl oleyl ammonium humate
50	Dimethyl di-(hydrogen tallow fatty alkyl) ammonium humate
	Methyl trilauryl ammonium humate
	Methyl tri-(hydrogen tallow fatty alkyl) ammonium humate
55	1 ¹ - hydroxyethyl, 2 ¹¹ - heptadecenyl, 2 - imidazolinium humate
	1 ¹ - benzyl, 1 ¹ - hydroxyethyl, 2 ¹¹ - heptadecenyl, 2 - imidazolinium humate

We use the term "alkyl ammonium" in the broad sense, wherein "ammonium" indicates an onium cation in which the basic atom is pentavalent nitrogen. Thus the term includes substituted ammonium cations in which two or more of the substituted positions may form part of a ring, as is the case in the

imidazolinium compounds listed above. It will be further understood that the above listing is illustrative and by no means exhaustive.

As the Examples in Table I shows, the present invention includes the employment of primary-secondary-tertiary-and quaternary-substituted alkyl ammonium cations, in all of which, of course, the nitrogen is pentavalent.

Generally, the compounds of our invention may be produced by bringing together humic acid and the alkyl ammonium compound in its base form. The base and the acid neutralize each other with salt formation, so as to produce an alkyl ammonium humate in accordance with the invention. Another general method of preparation is to convert the humic acid to a simple salt by reaction with an alkali, so as to produce sodium humate, potassium humate, or ammonium humate, by reaction with sodium hydroxide, potassium hydroxide, or ammonium hydroxide respectively. The alkyl ammonium compound is caused to be present in the form of a simple salt. Thus, a primary, secondary, or tertiary amine may be reacted with a simple acid e.g. hydrochloric or acetic, to give the corresponding substituted ammonium chloride or acetate, respectively. This method of procedure has the advantage that the simple substituted ammonium salts, and the simple humates as described, are both water soluble, so that aqueous solutions of each reactant may be made, and the reaction completed by mixing the solutions together. To give a simple example, octadecyl amine is treated with an equivalent quantity of acetic acid to give octadecylammonium acetate. This is then dissolved in several times its weight in water. Separately, humic acid is converted to sodium humate by treating lignite, for example, with sodium hydroxide to neutrality followed by filtering off the insoluble portion of the lignite. The solution of sodium humate thus formed is mixed with the solution of octadecylammonium acetate in stoichiometrically equivalent proportions, whereupon there occurs a quantitative precipitation of octadecylammonium humate. The equivalent weight of the humic acid can readily be determined in any known fashion applicable to acids generally, for example, by titration of sodium hydroxide using an electrometric pH meter.

A somewhat special case is presented by the quaternary substituted ammonium salts, which have no free base form. A simple example is trimethyl octadecylammonium chloride. In its quaternary salt form, it is already available for reaction with an alkali humate e.g. sodium humate, and it may also be reacted directly with humic acid, although the reaction is accelerated by adding some base e.g. sodium hydroxide to the reaction mixture to neutralize the acid which is formed as a result of the reaction, which in the particular example considered here would be

hydrochloric acid. The quaternary ammonium compounds may be in their hydroxide form, of course, and may then be reacted directly with humic acid.

The reaction methods just described are general, and are of general application except that in some cases the reaction does not always go to completion or proceed as rapidly as desired because of the physical state of the reactants, and we wish it to be understood that we contemplate that those practicing the invention will take into account the known methods of accelerating and especially of bringing to completion reactions of the type under consideration here. We shall not herein sufficient of such methods so as to enable anyone skilled in the art and desiring to practice the invention to do so, with any and all combinations of reactants within the purview of our invention.

Thus, for example, it is possible to select naturally occurring lignites which are nearly completely humic acid. If these are ground to, say, the fineness of passing a 200 mesh screen (U.S. Standard is used herein), and then mixed with an alkyl amine of the type described, our novel compounds will indeed be formed for a certain depth into each of the microscopic particles of lignite, but the very reaction product thus formed will considerably retard the penetration of additional amine into the interior of the lignite particle, so that unduly long times will be required for completing the reaction. If the reaction mixture just described is treated mechanically, so as to expose fresh portions of unreacted lignite, e.g. by the use of a paint mill or colloid mill, the reaction can be completed in a practicably short time. It will be apparent, therefore, that some methods of procedure are faster than others and therefore to be preferred, although in teaching the more preferable methods we do not wish to exclude the less preferable reaction conditions and combinations. The best method we know, generally is to make each of the reactants available in its salt form as hereinbefore described, and to react the two salts together in their aqueous solutions, whereby the reaction product is recovered as a precipitate and may be washed free of the simple salt which is a by-product of the reaction.

We will now give working Examples of our invention, which at the same time will serve to show the best method that we know for carrying it out. All percentages are by wt. and all mesh sizes are U.S. Standard, except where otherwise specified.

EXAMPLE 1

100 grams (dry weight) of lignite from Bowman County, North Dakota, characterized by a solubility of 85% (dry weight) in sodium hydroxide solution, was added to 1

litre of water and 30 grams of sodium hydroxide added. The solution was allowed to stand overnight with occasional stirring. The next day the pH was adjusted to 7.0 with sulphuric acid, and the supernatant liquid was decanted from the precipitate, which had a dry weight of about 15 grams. Separately, 90 gram of dimethyl dioctadecyl ammonium chloride were dissolved in 200 cc. of water, and this solution was added to the decanted sodium humate solution resulting from the first step. A flocculent precipitate of dimethyl dioctadecyl ammonium humate formed, which was separated by filtration on filter paper and washed with 200 cc. of distilled water. The produce was dried in a desicator over calcium chloride, and ground in a mortar to pass a 60 mesh screen. The reaction product was dispersible and soluble in organic solvents, e.g., benzene.

The Example just given shows the production of a quite pure product, free of the small amount of ash which is present in most lignite. For some purposes, it is not necessary to make a pure product, and we give a second working Example which produces a useful product at somewhat lower processing costs:

EXAMPLE 2

120.5 grams of the lignite described in Example 1 above, and containing 17% by wt. moisture, were mixed with 46.5 grams of water, 15.5 grams of dimethyl dioctadecyl ammonium chloride, and 8 grams of sodium hydroxide, and ground together with a mortar and pestle for three minutes. A product resulted which was useful as a dispersing agent in olephilic systems.

EXAMPLE 3

The reaction product of Example 2 was mixed in its entirety with 200 cc. of diesel oil in a Waring blender for 10 minutes. This produced a concentrated dispersion of dimethyl dioctadecyl ammonium humate in the diesel oil. This was useful in preparing oil-base drilling fluids and oil-base fracturing fluids of the type used in fracturing oil-bearing formations in order to increase the permeability thereof. For example, when the concentrate described was added to an additional quantity of diesel oil, in the proportions of 5 grams of the concentrate and 350 cc. of the diesel oil, a fluid was produced which when tested for fluid loss in accordance with the specifications of the American Petroleum Institute, Code No. 29, gave a 30-minute fluid loss of 2.6 cc., which is exceptionally low considering the low concentration of the additive present.

EXAMPLE 4

The process of Example 1 was carried out, except that instead of using dimethyl dioctadecyl ammonium chloride, 85 grams of lauryl amine and 26 grams of glacial acetic were

added to 200 cc. of water to form a solution of lauryl-ammonium acetate. This solution was mixed with the decanted sodium humate solution to give a flocculent precipitate of lauryl ammonium humate which was separated, washed, dried, and ground as described in Example 1. This product likewise was found to be readily dispersible in benzene, and indeed its solubility therein was demonstrated by the fact that solution so formed could be filtered through filter paper without decolorization, showing that the lauryl-ammonium humate was soluble therein.

All of the products described, as already mentioned, are dispersible in organic systems, and are useful as dispersing agents, for example, in dispersing finely grounded minerals in organic liquids, in the formulation of printing inks and in improving the dispersion of pigments in paints.

We have found that the reaction of the organic bases with humic acid results in the formation of a normal salt, with the stoichiometrically equivalent quantities of the components entering thereto. This is not to imply that only exactly stoichiometrically equivalent quantities may be used in practicing our invention. For example, if an excess of the base is used, then in addition to the alkyl ammonium humate which forms, some unreacted base will be present intermixed therewith; while if an excess of humic acid is used, the latter will be present as a diluent of the alkyl ammonium humate produced. The material which is active, however, in the practice of our invention, is the alkyl or alkenyl ammonium humate as defined above, and that is what we have accordingly recited in the claims which follow.

We have also found that the presence of an alkyl group or alkenyl group having 12 to 22 carbon atoms in a straight chain is necessary to impart the property of dispersibility and indeed solubility in organic liquid systems which characterizes the products of our invention.

The products of our invention are especially applicable in well-working fluids, including oil-base drilling fluids or "muds," oil-base emulsion drilling fluids, formation fracturing fluids, and well packer fluids. For example, in the rotary drilling of wells for oil and gas, drilling fluids are used which are circulated in such a manner as to remove cuttings and to support the walls of the hole. Most commonly such fluids are water base, comprising, for example, clay dispersed in water, but in recent years extensive use has been made of fluids having oil as the base, i.e., the continuous liquid vehicle.

The oily vehicle is converted into a drilling fluid having suitable properties for the task by adding various materials to thicken the oil so that it will support cuttings, to provide a low fluid loss when the fluid is subjected to filtra-

tion against a permeable formation, and in some cases to increase the density of the fluid. In accordance with this aspect of the invention, we provide a substituted ammonium humate in which at least one of the substituted radicals attached to the said ammonium is an alkyl radical having from 12 to 22 carbon atoms in a straight chain. The well working fluid of the invention not only provides a low fluid loss but also is useful in well-working operations where, for example, oil bearing sands of low permeability are commonly subjected to extremely high fluid pressures so as to crack them open, generally along bedding planes, and the fractures so formed are held open by solid propping agents introduced with the fracturing fluid. The well-working fluid of the invention serves admirably for this purpose and also, where it is necessary to fill the annular space between the casing and the walls of the hole. Here, likewise, our working fluid is advantageous in that it minimizes corrosion and provides low fluid loss properties so that the packing fluid remains in place over a long period of time.

In the earlier development of oil base fluids of the types described, primary attention was given to providing thickening additives. Many were found and have been used at various times, including carbon black, soaps of fatty acids, rosin, tall oil, and like organic acids and asphalts of various kinds. In recent years, however, it has become apparent that a low fluid loss is the most important characteristic of these fluids to be sought for, and that thickening to whatever degree desired can generally be readily accomplished by any of several means, provided that the fluid loss is maintained at a very small value. The fluids in accordance with our invention are characterized by extremely low filter loss, and the additives which we use in practicing our invention are of such nature that undue thickening does not set in before the fluid loss is lowered to a satisfactory level, as more and more of the additives is introduced, all as set forth in greater detail hereinbelow.

Generally, and in accordance with an illustrative embodiment of our invention, we treat an oily liquid, which is most desirably diesel oil but may also be any available crude oil, topped or untopped, or various fractions of crude oil, including kerosene and fuel oil, with a salt of humic acid, viz., a humate of the type hereinbefore described.

The treatment of the oily liquid, viz., the petroleum oil, with the humic acid salt described hereinabove is carried out by simply mixing the selected humic acid salt in the oily vehicle, using sufficient of the humic acid compound to reduce the filter loss of the oil to the desired degree. This, of course, will vary somewhat depending upon the nature of the well drilling or treating or working

conditions involved. As a general guide, however, we find that it is desirable to add enough of our long-chain ammonium humate compound to the oil so as to achieve a filter loss of not exceeding 5 cc. when the test is made for 30 minutes in accordance with Code RP 29 of the American Petroleum Institute. This test is well known in the industry, and involves the use of a pressure filter of three inches diameter operating at 100 pounds per square inch gauge. The filtrate connected in a 30-minute test is a measure of the filter loss of the fluid. Generally, such a low filter loss is achieved by the use of from 2 to 20 pounds of long-chain alkyl ammonium humate per barrel of well-working fluid. Of course, for special field conditions very low filter losses may be needed, and as much as 50 pounds per barrel may then be used.

The well-working fluids made in accordance with our invention may also include the additives known to the art. These comprise weighting materials, which include finely ground clay, limestone, silica, barite, and celestite. Where the well-working fluid is used in fracturing, propping agents e.g. sand, aluminium spheres and walnut shells, will normally be included. Whenever incorporation of the long-chain alkyl ammonium humate to the extent needed to achieve a fluid loss equal to or less than 5 cc. does not serve to thicken the fluid as much as desired, then other known thickening agents may be used. Such thickening agents are the asphalts, particularly air-blown asphalts as described in Lawson *et al.* United States Patent No. 2,223,027; soaps e.g. sodium and/or calcium oleate, stearate and tallate. Water may also be readily incorporated into the well-working fluids of our invention, and serves as an inexpensive method of increasing the density of fluids whenever they are less dense than water itself. The water is taken up in the form of a water-in-oil emulsion, so that the continuous liquid phase of the fluid is still oil. Anywhere from 1% to 30% by volume of water may readily be incorporated in our fluids.

It is convenient, and generally facilitates the addition and incorporation of the long-chain alkyl ammonium humate into the oil, to provide the humate already dispersed in materials which is compatible with the fluid just made, and indeed will generally be a portion of the oil itself. Thus, a concentrate may be prepared of the humate and diesel oil in any desired weight ratio, say 1:10; and this will generally be an easier form for adding the humate. Alternatively, if a weighting material is to be used, for example, pulverized limestone, the powdered humate may be premixed with the latter in, say, a 1:5 weight ratio.

We give now a working Example.

EXAMPLE 5

An alkyl ammonium humate well-fluid treating concentrate was prepared as follows: 658 pounds of the lignite from Bowman County, North Dakota, having a solubility of 85% (dry weight) in an aqueous solution of sodium hydroxide containing 17% by wt. moisture, was introduced into a pug mill together with 98 pounds of powdered caustic soda, 156 pounds of water, 136 pounds of commercial dimethyl di(hydrogenated tallow alkyl) ammonium chloride, and 52 pounds of diesel oil. Reaction took place to give a dimethyl di(hydrogenated tallow alkyl) ammonium humate, which was fed into a tank containing 800 pounds of additional diesel oil, where it was agitated by pumping, with the addition of 100 pounds of additional water, to give a pourable concentrate.

This concentrate was taken to a well site and mixed as follows:

1330 lbs. concentrate

80 bbls. diesel oil

1720 lbs. sulphurized tall oil*

350 lbs. caustic soda

160 lbs. calcium chloride

*prepared by mixing 6 parts sulphur with 92 parts tall oil, heating for three hours at 275° F., cooling, and adding 25 parts kerosene.

The function of the sulphurized tall oil was to form a soap with the caustic soda and calcium chloride, which imparted the desired consistency to the "mud," or oil-base drilling fluid.

The fluid thus prepared has an API fluid loss of 0.0 cc., and a viscosity of 39 centipoises API. This fluid was used in drilling the well with a core-drill. The cores recovered showed only 1/8" of filtrate invasion, which was remarkably low.

WHAT WE CLAIM IS:—

1. A substituted ammonium humate having the formula $R_1R_2R_3R_4N^+Hu^-$ in which the Hu^- is the anion of humic acid and in which at least one of the R 's is an alkyl or alkenyl radical having from 12 to 22 carbon atoms in a straight chain, and in which those R 's which do not have from 12 to 22 carbon atoms in a straight chain comprise hydrogen, alkyl radicals having fewer than 12 carbon atoms, phenyl or benzyl, or two of the R 's form a carbon ring including N heterocyclically and bearing said 12 to 22 carbon atom alkyl or alkenyl radical, and wherein the two of the R 's form a nitrogen-containing heterocyclic range of the remaining R 's additionally may be a hydroxyalkyl or phenyl-substituted hydroxy-alkyl group.

2. The process of preparing a substituted ammonium humate, as defined in claim 1 characterised by the fact that an appropriate substituted ammonium ion having the formula $R_1R_2R_3R_4N^+$ is caused to react with a negative humate ion so as to form the said substituted ammonium humate.

3. The process according to claim 2, wherein said humate ion is derived from a brown coal.
- 5 4. The process according to claim 2, or 3, wherein said substituted ammonium ion and said humate ion are caused to react in substantially stoichiometric proportions.
- 10 5. The process of treating an oleaginous oil well working fluid so as to reduce its filter loss, characterized by adding thereto a substituted ammonium humate as defined in claim 1.
- 15 6. The process according to claim 5, wherein said oleaginous oil well working fluid comprises an oily base of a liquid petroleum.
7. The process according to claim 6, wherein in addition to said liquid petroleum, said fluid includes a soap, a weighting agent and water.
- 20 8. The process according to any one of claims 5 to 7, wherein said substituted ammonium humate is present in a concentration within the range of 2 to 50 pounds per barrel.
9. The process of preparing a substituted ammonium humate according to claim 2 and substantially as hereinbefore described. 25
10. A substituted ammonium humate whenever prepared by the process of any one of claims 2 to 4.
11. A substituted ammonium humate as defined in claim 1 and substantially as hereinbefore described. 30
12. The process of treating an oleaginous oil well working fluid according to claim 5 and substantially as hereinbefore described. 35

STEVENS, LANGNER, PARRY
& ROLLINSON,
Chartered Patent Agents,
Agents for the Applicants.